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16. ABSTRACT

The authors provide an overview of thermal treatment, a discussion of EPA incineration regulations, and discussion of several specific thermal processes. Included are discussions of rotary kilns, liquid injection systems, industrial boilers, industrial processes using waste as fuel ocean incineration, and new thermal processes. The discussion addresses how the systems work, what the capabilities of the system are, and to what extent they are being utilized. The paper is of interest to those interested in a broad overview of incineration today.

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THERMAL DESTRUCTION OF HAZARDOUS WASTE — A STATE-OF-THE-ART REVIEW

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Summary

The treatment and destruction of organic hazardous waste streams through use of incinerators and other thermal processes is and will continue to be an important waste management option in the U.S., Canada, and other industrial countries. In this paper, the authors discuss incineration, pyrolysis systems, boilers, and industrial processes, and various innovative systems. In addition to containing various process descriptions, the paper also contains relevant regulations and the results/environmental assessments carried out by the EPA. The overall purpose of the paper is to provide a review of those thermal options currently of interest to the waste management community.

Introduction

As the land disposal of untreated hazardous wastes becomes less acceptable in the eyes of not only the environmental community, but also in the eyes of the public in general, increasing attention is being given by industry and government to alternative hazardous waste treatment and destruction processes. Among these processes are high-temperature incinerators and other thermal process that treat waste streams by exposing the wastes to high temperatures.

Thermal processes can, in a matter of seconds or minutes, destroy or significantly reduce the volume of wastes that might otherwise take months or years to degrade in a landfill. Thermal processes can greatly reduce environmental and health hazards associated with land disposal, reduce the need for new landfill capacity, and eliminate the possibility of problems literally resurfacing in the futre [1].

In its May 1980 Hazardous Waste and Consolidated Regulation, the U.S. EPA states:

> "Incineration is a relatively well-developed and well-understood technology. Properly executed, it can accomplish safe destruction of primarily organic hazardous waste, permanently reducing large volumes of waste materials to non-toxic gaseous emissions and small amounts of ash and other residues. Incineration can often provide an optimum, permanent solution to hazardous waste management with minimal long-term ecological burden." [2]

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Thermal process overview

Thermal processes are processes for reducing the volume and/or toxicity of organic wastes by exposing them to high temperatures in controlled environments designed to encourage material breakdown. When the waste streams are subjected to temperatures of from 800°F to 3000°F (430—1530°C) they tend to break down into simpler and less toxic forms. Generally speaking, thermal processes consist of high-temperature incinerators, pyrolysis systems, boilers, and industrial processes. An "other" category might include those mostly newer processes that utilize high temperatures as a destruction medium, but differ substantially from the more conventional thermal processes. Table 1 summarizes the characteristics of each type of the conventional process. The newer processes are discussed individually later in the paper.

TABLE 1

Thermal processes

Incinerators	—	Devices designed primarily to destroy materials by exposing them to high temperatures in a turbulant environment for a sufficiently long time to bring about oxidation through combustion.
Pyrolysis systems	—	Devices that expose materials to high temperatures in an oxygen-starved environment. Waste materials are pyrolysized in a reducing atmosphere that produces combustible off gases.
Boilers (hazardous waste as fuel)	—	Boilers are devices designed to produce steam through the combustion of fossil fuels. They are considered to be a thermal hazardous waste process when hazardous waste is used as a supplemental fuel.
Industrial processes	—	Those industrial processes such as cement production, lime production, blast furnaces, and sulphuric acid regeneration plants that use hazardous wastes as a supplemental fuel, fired directly into the production area of the process.

EPA regulations

As treatment devices for wastes listed as hazardous by the Resources Conservation & Recovery Act (RCRA), incinerators are covered by Federal Regulations.

On January 23, 1981, EPA promulgated regulations for the incineration of RCRA hazardous wastes. These regulations state:

- A destruction and removal efficiency (DRE) of 99.99 percent must be achieved for each principal organic hazardous constituent (POHC) designated in the waste stream.
- Particulate emissions may not exceed 180 mg/dscm (0.08 grains/dscf) for a stack gas corrected to 7 percent oxygen.
- Stack emissions of hydrogen chloride (HCl) must be no greater than the larger of either 1.8 kg per hour (4 lb/h) or 1 percent of the HCl in the stack gas prior to entering any air pollution control equipment [3].

A POHC is a substance which is listed by EPA as a hazardous waste in Appendix VIII of the Federal Register (40 CFR Part 261, May 19, 1980) or a waste which is determined to be hazardous because it fails one or more of EPA's waste characteristic tests (ignitible, toxic, corrosive, reactive). For wastes which are made up of only one hazardous component, the single compound is the POHC. For mixtures of compounds, EPA provides guidance that recommends selecting as POHCs those compounds which are present in the waste in the highest concentration and also those compounds which are the most difficult to destroy through incineration. For cases where data on "incinerability" (degree of difficulty of achieving the 99.99 percent DRE) is lacking, EPA recommends using the compound unit heat of combustion (HC per molecular weight (*MW*) as an incinerability ranking procedure (the higher the HC/*MW*, the easier the compound is to destroy) [4].

EPA's regulations provide for certain exceptions to the incineration standard. Wastes that are hazardous solely due to the characteristic of ignitibility are exempt from the regulations. Finally, as stated previously, wastes that are burned in any device that functions primarily to produce energy are considered fuels, not RCRA hazardous wastes, and are exempt from the incinerator requirements. EPA is considering regulations for these boilers and industrial thermal processes. The Agency has issued guidelines that will help permitting officials determine if a given thermal operation is, indeed, a legitimate energy production process, or merely a "sham" to evade the regulations. These guidelines deal with fuel value of the waste, the disposition of the energy produced, and the ratio of waste to primary fuel in the combustor.

EPA has proposed a regulation for limitation of hazardous combustion by-products, or products of incomplete combustion (PICs) but the proposal has not yet been promulgated into a regulation. In addition, RCRA regulations require minimum operating controls such as preheating the combustion chamber with fossil fuel before waste is introduced, automatic waste cut-off in the case of combustor "upset" and continuous monitoring of carbon monoxide, flame activity, and combustion gas temperature. Exact control parameters for each individual facility are determined during the permitting process and most often established through a trial burn.

Incineration of polychlorinated biphenyls (PCBs) is regulated under the

Toxic Substances Control Act (TSCA). These regulations require a destruction efficiency of 99.9999 percent. In addition, design specifications for burner operation are imposed. A combustion temperature of 1200 ± 100°C (2200 ± 212°F) and a gas residence time of 2 s are required [5].

Burning wastes at sea in ocean-going-incinerator ships is regulated per international agreement [6]. Current requirements are for a 99.9 percent destruction efficiency but any permits that may be granted most likely will require performance equivalent to RCRA and/or TSCA provisions for POHC destruction. The ships usually do not have air pollution devices and could not operate if requirements are imposed for HCl control.

Thermal process technologies

Although there are many thermal processes in various stages of development in the country today, there are only five technologies that have been used to treat significant amounts of waste. These are liquid injection incinerators, rotary kiln incinerators, industrial boilers, cement kilns, and ocean incinerator ships.

Liquid injection incinerators

A liquid injection system consists of one or more refractory-lined combustion chambers and a series of atomizing nozzles. It is capable of burning virtually any combustible waste that can be pumped. Wastes to be burned are usually blended in mixing tanks prior to atomization to improve either their pumpability or combustability, and then are atomized and burned in suspension. The capacity will vary depending upon the energy value of the wastes. Typical combustion chamber residence times and temperatures are 0.5—2 s and 700—1650°C, respectively. In addition to being the primary part of a waste combustion system, a liquid injection incinerator is often used as an afterburner to complete the combustion of waste gases following burning in other incinerators such as rotary kilns [1].

The advantages of liquid injection units include their capability to incinerate a wide range of wastes and their relatively low maintenance costs due to the few moving parts in the system. The primary disadvantage is that they can burn only pumpable liquids, and are susceptile to being shut down because of clogged nozzles. Liquid injection systems are also usually designed to burn specific waste streams and consequently are not often used for multi purpose facilities.

These facilities have been used to destroy a variety of wastes including phenols, PCBs, still and reactor bottoms, solvents, polymer wastes, herbicides, and pesticides. They are not recommended for burning heavy metals, high-moisture content wastes, or materials with high, inorganic content.

Liquid injection is a technology in daily use throughout the country both at industrial locations and at central treatment facilities. It is the most commonly-used incinerator for hazardous waste destruction, comprising some 64% of the market for incinerators [7].

Rotary kiln incinerators

The rotary kiln system is the most nearly universal of waste disposal systems. It can be used for a wide variety of solid and sludge waste disposal, and for the incineration of liquid and gaseous wastes [8].

Rotary kiln incinerators are refractory-lined cylinders mounted with their axes inclined at a slight angle from the horizontal. This type of incinerator has a length-to-diameter ratio between 2 and 10; a rotational speed in the range of 1 to 5 fpm (measured at kiln periphery); an incline ratio between 1/16 and 1/4 in./ft; an operating temperature upper limit of 3000°F (1650°C), although typical temperatures are lower; a residence time that can vary from seconds to hours. It can be used to dispose of solids, sludges, liquids, and gases. The speed of rotation may be used to control the residence time and mixing with combustor air.

The primary function of the kiln is to convert, through partial burning and volatilization, solid wastes to gases and ash/residue. The ash is removed and, if found to be free of unacceptable levels of hazardous wastes, is put in a landfill. An afterburner using gaseous or liquid fuels or wastes to generate a high-temperature oxidizing environment is almost always required to complete the gas-phase combustion reactions. The afterburner is connected directly to the discharge end of the kiln, where the gases exiting the kiln turn from a nearly horizontal flow path to a vertical flow path upwards to the afterburner chamber. The afterburner itself may be horizontally or vertically aligned [9].

The system is designed so that a negative pressure can be maintained in the kiln in order to minimize emissions at the end seals of the rotating section.

Both the afterburner and kiln are usually equipped with an auxiliary fuel firing system to bring the units up to the desired operating temperatures. The auxiliary fuel system may consist of separate burners for auxiliary fuel, dual-liquid burners designed for combined waste/fuel firing, or single-liquid burners equipped with a premix system. Fuel flow is gradually turned down, and liquid waste flow is initiated after the desired operating temperature is attained [9].

In rotary kilns, liquid wastes may be fired either at the feed or discharge end of the unit; cocurrent and countercurrent firing designs are both used. Rotary kilns have the advantages of being able to incinerate a wide variety of liquid and solid wastes, being able to accept drum and bulk containers, and being able to retain waste materials sufficiently long to accomplish very high destruction rates. Rotary kilns are capital intensive and need significant maintenance to maintain seals and refractory [1].

Industrial boilers

There are over 240,000 industrial boilers in the United States. Under current U.S. EPA RCRA regulations, hazardous materials can be burned in any of these boilers without being subject to the incinerator performance

standards. More likely to be used for waste disposal are the over 5,500 boilers that have heat production capacities of 1.0×10^{10} J/h (10^7 Btu/h) or greater in the chemicals, petroleum refining, and paper industries [10].

Boilers that have been or could be used for hazardous industrial waste disposal include small firetube gas- or oil-fired units in the $1.0—5.3 \times 10^{10}$ J/h ($1.0—5.0 \times 10^7$ Btu/h) range, package gas- or oil-fired watertube units in the $5.3—15.8 \times 10^{10}$ J/h range ($5.0—15.0 \times 10^7$ Btu/h) and large field erected oil or coal boilers larger than 15.8×10^{10} J/h (15.0×10^7 Btu/h). Wastes that are fired generally are liquid wastes that are generated on the site of the facility (or plant) that contains the boiler. Wastes that are burned include alcohols, spent nonhalogenated solvents, and highly volatile by-products which may be gaseous when introducted into the boiler.

For the smaller boilers with only one burner, conventional practice is to premix the primary fuel (oil) and the waste material in a tank prior to introduction into the firebox. For larger boilers with multiple burners, one or more burner is dedicated to waste introduction with the remaining burners fired with primary fuel and used for leveling.

Waste may constitute over 50 percent of the fuel to the boiler for particularly clean, high energy value wastes. However, generally, the waste feed rate is below 20 percent of the total fuel to the boiler. For difficult-to-burn wastes and, particularly for corrosive halogenated wastes, feed concentrations below 5 percent (on a volume basis) are most common.

Small industrial boilers (less than 1.58×10^3 J/h) in the United States are not currently subject to Federal air pollution control regulations. Therefore, most industrial gas- or oil-fired boilers do not have air pollution control devices. Larger pulverized coal-fired boilers do generally have ESPs for particulate control. Smaller stoker-coal boilers may have mechanical cyclone collectors for large particles. Some boilers which are specifically designed to fire halogenated wastes may have wet scrubbers but there are very few, if any, industrial boilers which fire waste on a retrofit basis that have such control devices.

As part of its process to determine if a Federal regulation is required for boiler disposal of hazardous wastes, EPA has conducted field tests of several operating facilities. Generally, the tested boilers have achieved performance in the vicinity of 99.99 percent DRE, not quite as good as incinerators, but not as bad as the Agency feared at the outset of the test program. Emissions of products of incomplete combustion from boilers, as might be expected due to the reaction product quenching in the superheaters and through the steam tubes, have been 50 to 20 times higher than emissions of principal organic hazardous constituents from the boilers [11].

The greater advantage of boiler disposal is its reduced cost to the waste generator over either onsite or offsite incineration. Besides realizing the fuel value of the waste, the generator appreciates a sizable opportunity cost savings from not having to dispose of the waste material in a RCRA regulated process. Also, the waste material does not have to be transported, at

some environmental risk, to a waste disposal site, which, under RCRA, prolongs the waste generator's liability for the waste material.

The biggest disadvantage of boiler disposal is the fact that the process is not currently regulated and may be prone to abuse by operators. It also deprives incinerator operators of a prime fuel material and may contribute to an increase in the cost of commercial incineration of RCRA hazardous wastes [10].

Cement kilns

An integral part of the process for manufacturing cement is exposing limestone and several additives to temperatures above 2600°F (1430°C) in a large rotary kiln fueled with a fossil fuel. The end product of this process is a solid material called clinker. Ground-up clinker is the major constituent of cement. Since the combustion conditions in cement production are much more severe than those present in many waste incinerators, cement kilns are considered to be a promising disposal option for many organic wastes. They are considered especially applicable for incinerating chlorinated wastes since the hydrochloric acid produced serves to neutralize the clinker production process which is normally alkaline.

In test burns carried out in Canada, Sweden and the United States, it has been determined that hard-to-burn wastes such as PCBs can be successfully combusted in cement kilns [12]. Less hazardous chemicals such as waste solvents and still bottoms from solvent reclaiming operations are already being purchased by cement companies and burned on a continuous basis in cement kilns [1].

There is ample opportunity to employ cement kilns as disposal vehicles in the United States. The United States cement industry has 158 plants and 342 operating kilns. Plant capacities range from 50,000 to 2,200,000 tonnes per year of cement product. Plants tend to be located near large population centers and, therefore, close to the sources of waste generation. Unlike boilers however, cement kilns are not located on the premises of the waste generator and the waste must be transported offsite for disposal. There is significant economic incentive for a kiln operator to accept wastes for disposal. Besides obtaining a fee for disposal of the wastes, the operator can offset some of the 33 to 40 percent of the total cost of cement manufacture that is attributed to energy demand [10].

The advantages of using cement kilns are that, in addition to the wastes being destroyed, the energy value of the waste is reclaimed, the capacity of the cement industry to consume chemical wastes is quite large, and cement plants are already located near many waste-generating sources. The disadvantages are that burning chlorinated wastes in cement kilns appears to increase the production of particulates, requiring more extensive air pollution control devices, utilizing wastes as fuel in plants not used to handling wastes requires an upgrading of the facilities. The EPA has estimated that there exists enough cement-making capacity within the largest waste-pro-

ducing states to incinerate all of the chlorinated wastes produced in those states [1]. The California Air Resources Board recently recommended the use of cement kilns as a means of destroying PCB wastes [13].

Ocean incineration [10]

Incineration-at-sea is a technically viable process [14]. There are currently two ships operating in Europe. Ships have operated intermittently off the United States Gulf Coast burning specialized wastes. One ship has applied for a permit for continuous operation off the United States coast and at least two United States ships have been constructed.

Incinerator ships are, in essence, large floating liquid injection incinerators. The ships consist of crews' quarters, storage tanks, and incinerators. The ships generally have two or three incinerators. Unit incinerator sizes can be as much as 50 percent larger than the largest land-based liquid injection incinerators. A single ship can handle as much as 6000 metric tonnes of liquid hazardous wastes per voyage.

The incinerator ships do not use flue gas scrubbers, even for highly halogenated wastes. The premise behind the absence of scrubber is that the plume will touch down in the ocean and the sea water will serve as a buffer for the acid gas. If the incinerator ships were required to incorporate scrubbers, the cost advantage they accrue due to their larger capacities than land based units would be diminished. Incinerator ships require, of course, shore-based facilities for collecting, storing, blending, and loading the wastes.

The U.S. PEA has conducted performance tests during a number of waste burns. Waste destruction efficiencies (DEs) were found to be equivalent to those achieved by land-based incinerators [15,16].

The main advantages of at-sea incineration are the large waste handling capacities, low unit disposal costs, and the alleviation of incinerator siting problems by removal of the burn site from land. Disadvantages include the inability to handle solids and sludges, the need for the shore facilities, and the lack of HCl control [10].

Thermal processes in the U.S.

Incineration and other thermal processes have been used as a final treatment or disposal method for hazardous wastes in the United States for one or two decades at least. In 1984, it is estimated that there are some 230 industrial or government-owned incinerators which incinerate about 1.70 million metric tonnes of hazardous waste per year. This incinerated waste tonnage, however, is a very small portion of the current estimated 264 million metric tonnes per year of waste generated, of which perhaps 25.0 million liquids is 150 gallons per hour (570 l/h), while the median capacity of solids

According to EPA's information [18] about 80 percent of the existing 230 incinerators are privately owned and operated, while 20 percent are commercial or military operations. That is, 80 percent are primarily de-

dicated to incinerating wastes from the private industrial companies which own and operate these incinerators on their own property. As to the generic designs of all incinerators, EPA believes that about 48 percent are liquid injection units, 19 percent are fixed hearths, 6 percent are rotary kilns, and 27 percent are various military, fluid bed, or undetermined designs at this point. Additionally, the majority of units have been installed within the past ten or fifteen years. The median capacity of individual incinerators for liquids is 150 gallons per hour (570 l/h), while the median capacity of solids units is about 650 pounds per hour (295 kg/h) [17].

The total incinerator design and marketing community consists of about 57 companies, although the majority of units installed have been sold by about 20 firms. EPA understands that 45 percent of all units have air pollution control systems, 22 percent have heat recovery capability, and generally the thermal operating conditions involve combustion temperatures of 1800°F (980°C) or higher [17].

Considerable amounts of hazardous wastes are also being thermally destroyed in industrial boilers or other high temperature thermal processing equipment such as cement kilns, etc., in addition to incinerators. In 1984, for example, compared to the 1.7 million tonnes per year noted above for incinerators, an additional 3.85 million tonnes per year were managed or processed through boilers and kilns, etc. The incentives for routing wastes to boilers and other industrial processes include utilization of the heating value of certain high-energy content hazardous waste streams as well as current regulatory exemptions under RCRA associate with reuse or recycling of waste [17].

No hazardous waste from the U.S. is currently being incinerated in ocean incinerators. However, the EPA is considering applications for permits [19].

New thermal processes

During the past decade several innovative thermal processes have been developed that varied significantly from convential incineration in one or more ways. An extensive survey of all of these processes is beyond the scope of this paper. The six processes briefly discussed herein will provide the reader with a flavor of the types of new thermal processes that are becoming an increasingly important part of the thermal processes state-of-the-art. None of these new processes is currently being used to incinerate a significant percentage of the waste stream. The six innovative thermal processes are:

- High temperature electric reactor
- Molten salt
- Plasma arc
- Wet air oxidation
- Molten glass incineration
- Supercritical water

High temperature electric reactor

This process utilizes a vertical reactor heated by electrodes implanted in the walls to pyrolize organic wastes. The process is offered by two companies, Thagard Research, which developed the process, and Huber Corporation, which acquired rights to the process and introduced several modifications.

The process utilizes a reactor with a core enclosed by porous refractory material. Carbon electrodes implanted in the wall of the reactor heat the reactor core to radiant temperatures. Heat transfer is accomplished by radiation coupling. A geaseous blanket formed by flowing nitrogen protects the porous walls. In the process organic compounds are rapidly heated to temperatures in the range of 3800—4400°F (2090—2430°C) and destroyed.

In the Huber process product gas and waste products pass through two-post reactor treatment zones which provide for additional exposure to high temperatures and for product gas cooldown.

The process is designed to pyrolize organics attached to particulates such as carbon black or soil. However, the developer claims that recent tests have shown the process is also effective for liquid refractory waste streams such as carbon tetrachloride.

The unit will process from 75 to 125 pounds (34—57 kg) of contaminated solids per minute. Hard numbers are not available for pure liquids. However, capacity would be less [20].

Molten salt

Molten-salt destruction is a method of burning organic material while, at the same time scrubbing in-situ any objectional by-products of that burning and thus preventing their emission in the effluent gas stream. This process of stimulating combustion and scrubbing is accomplished by injecting the material to be burned with air or oxygen-enriched air, under the surface of a pool of molten sodium carbonate. The melt is maintained at temperatures on the order of 900°C, causing the hydrocarbons of the organic matter to be immediately oxidized to carbon dioxide and water. The combustion by-products, containing such elements as phosphorous, sulfur, arsenic and the halogens, react with the sodium carbonate. These by-products are retained in the melt as inorganic salts rather than being released to the atmosphere as volatile gases. In time, inorganic products resulting from the reaction of organic halogens, phosphorous, sulfur, etc., build up and must be removed from the molten bed to retain its ability to absorb acidic gases. Ash introduced by the waste must be removed to preserve the fluidity of the melt. An ash concentration in the melt of about 20% by weight provides an ample margin of safety to maintain melt fluidity.

The molten salt process is designed for solid and liquid waste streams. It is especially applicable to highly toxic wastes and to highly halogenated waste streams. Waste streams with high percentages of ash and non-combustibles are not very good for the system since such waste makes it necessary to replace the molten bed more often.

A new pilot scale facility capable of processing 80 to 200 pounds of waste per hour (36—91 kg/h) has recently been constructed by Rockwell International. No commercial scale units have been built to date [20].

Plasma arc technology

One of the emerging technologies receiving much attention is plasma arc technology, which is a process using the extremely high temperatures of plasma to destroy hazardous waste.

A plasma is a substance consisting of charged and neutral particles with an overall charge near zero. A plasma arc is generated by electricity and can reach temperatures up to 50,000°F (27,760°C). When applied to waste disposal, the plasma arc can be considered as an energy conversion and energy transfer device. The electrical energy is transformed into a plasma. As the activated components of the plasma decay, their energy is transferred to the waste materials exposed to the plasma. The wastes are ultimately decayed and destroyed as they interact with the decaying plasma.

In a mobile prototype of a patented process a 500 kW plasma device is fitted to one end of a stainless steel reaction chamber and mated to a hollow graphite core to form an atomization zone. Residence time in this atomization zone is approximately 500 μs. The reaction chamber serves as the equilibration zone where the atomized species recombine to form new simple nonhazardous products. This zone is equilibrated at a temperature range of 1200—1800 K and the residence time in this zone is approximately one second. All hardware is designed to be located within a forty-five-foot-long (13.7 m) moving van type trailer.

Plasma arc technology is designed for highly toxic liquid waste streams. The operation of the process is not significantly impacted by the degree of halogenation of a waste stream.

A unit currently being demonstrated through partial support of U.S. EPA will process 600 pounds of waste per hour (270 kg/h). This unit is sized to be operated commercially [20].

Wet air oxidation

Wet air oxidation is a process for oxidizing organic contaminants in water. Wet air oxidation refers to the aqueous phase oxidation of dissolved or suspended organic substances at elevated temperatures and pressures. Water, which makes up the bulk of the aqueous phase, serves to modify oxidation reactions so that they proceed at relatively low temperature (175—340°C) and at the same time serves to moderate the oxidation rates removing excess heat by evaporation. Water also provides an excellent heat transfer medium which enables the wet oxidation process to be thermally self-sustaining with relatively low organic feed concentrations.

An oxygen-containing gas, usually air, is bubbled through the liquid phase in a reactor used to contain the process, thus the commonly used term "wet air oxidation" (WAO). The process pressure is maintained at a level high

enough to prevent excessive evaportion of the liquid phase, generally between 300 and 3000 psi.

A wastewater stream containing oxidizable contaminants is pumped to the system by means of a positive displacement-type pump. The wastewater passes through a heat exchanger which preheats the waste by indirect heat exchange with the hot oxidized effluent. The temperature of the incoming feed is increased to a level necessary to support the oxidation reaction in the reactor vessel. Air and the incoming liquid are injected into the reactor where the oxidation begins to take place. As oxidation progresses up through the reactor, the heat of combustion is liberated, increasing the temperature of the reaction mixture. This heat of oxidation is recovered by a heat exchange that utilizes the incoming feed. Thus it is thermally a self-sustaining operation. After energy removal, the oxidized effluent, comprosed mainly of water, carbon dioxide, and nitrogen is reduced in pressure through a specially designed automatic control valve.

Of all variables affecting wet air oxidation, temperature has the greatest effect on reaction rates. In most cases, about 300°F (150°C) is the lower limit for appreciable reaction, about 482°F (250°C) is needed for reaction to the 80 percent reduction of chemical oxygen demand (COD) range, and at least 572°F (300°C) is needed for 95 percent reduction of COD or better reaction within practical reaction time.

The use of catalysts have been evaluated for improving the destruction efficiency of WAO. However, there are no commercial application of WAO utilizing a catalyst at the present time.

The process is designed primarily for very dilute aqueous wastes which are too dilute to incinerate economically yet too toxic to treat biologically. WAO also has application for inorganic compounds combined with organics. It is not very effective in oxidizing highly refractory chlorinated organics

An existing unit is being demonstated on various waste stream at Casmolia, California. This unit can process up to 38 l/min (10 gal/min) [20].

Molten glass incineration

The integral part of this process is an electric furnace approximately 22 ft (6.7 m) long and 3 ft (0.9 m) wide that has a pool of molten glass covering the bottom. This type of furnace is used extensively in the glass manufacturing industry to produce glass. When used as a waste incinerator the extremely high temperatures in the combustion chamber destroy organic waste streams.

Waste materials, both combustible and non-combustible, are charged directly into the combustion chamber above the pool of molten glass. The waste can either be contained in fiberboard boxes, or uncontained in loose form. Electrodes immersed in the pool maintain the temperature of the pool of molten glass above 2300°F (1260°C). Combustible wastes are oxidized above the pool, and inorganics and ash fall onto the pool where they are melted into the glass. Combustion off-gases pass through ceramic filters

which are themselves charged into the molten glass when they are no longer effective.

Any combustible waste is acceptable. Degree of halogenation is not a consideration. However scrubbers will be required for HCl emissions.

Since this technology is used in the glass manufacturing industry, existing units are capable of processing from 100 pounds per hour (45 kg/h) to 21,000 pounds of raw materials per hour (9525 kg/h). However, these have not yet been demonstrated as devices for destroying hazardous wastes [20].

Supercritical water

In the supercritical water process an aqueous waste stream is subjected to temperatures and pressures above the critical point of water, i.e. that point at which the densities of the liquid and vapor phase are identical. (For water the critical point is 379°C and 218 atm). In this supercritical region water exhibits unusual properties that enhance its capability as a waste destruction medium. Because oxygen is completely miscible with supercritical water, the oxidation rate for organics is greatly enhanced. Also inorganics are practically insoluble in supercritical water. This factor allows the inorganics to be easily removed from the waste streams. The result is that organics are oxidized extremely rapidly and the resultant stream is virtually free of inorganics.

A patented process has been developed that incorporates the properties of supercritical fluids to oxidize organic contaminants in aqueous streams. The following is a brief summary of the process:

a. Waste is slurried with make-up water to provide a mixture of 5 percent organics. The mixture is heated using previously processed supercritical water and then pressurized.
b. Air or oxygen is pressurized and mixed with the feed. Organics are oxidized in a rapid reaction. (Reaction time is less than 1 minute.) For a feed rate of 5 percent by weight of organics, the heat of combustion is sufficient to raise the oxidizer effluent to 500°C.
c. The effluent from the oxidizer is fed to a salt separator where inorganics are removed by precipitation.
d. Waste heat from the process can be reclaimed to provide sufficient energy for power generation and high pressure steam.

Supercritical water processes are designed for aqueous waste streams with high levels of inorganics and toxic organics. The system's capability for treating aqueous waste streams with high percentages of halogenated material has not yet been demonstrated [20].

Fluidized-bed incineration

Fluidized-bed incinerators are thermal processes using a very turbulent bed of inert granular material to improve the transfer of heat to the waste streams to be incinerated. Advantages of fluidized-bed incinerators include their relatively compact design, their relative simplicity of operation, and

their ability for combining combustion with pollution control by trapping some gases in the bed. Although fluidized beds have been used for many years in various industries, their use in hazardous waste incineration is still at a demonstration level. It is generally agreed, however, that this approach to waste incineration offers significant potential for the future.

One of the more innovative fluidized-bed incinerators currently in operation is the circulating-bed system. The circulating-bed concept is distinct from conventional fluidized beds, which have a fixed bed depth and operate within a narrow range of gas velocities (between the minimum and maximum fluidization velocities). At velocities beyond the maximum, the bed material becomes entrained, with carryover of unburned particles from the combustion chamber. At velocities below the minimum, the bed may slump.

In the circulating bed concept, combustible waste is introduced into a non-mechanical seal along with recirculated bed material from the hot cyclone. Both the fresh feed and the recirculating material are fed into the combustion chamber. A high air velocity 5 to 6 m/s (15 to 20 ft./s) entrains both the bed and the combustible waste, which rise through the reaction zone to the top of the combustion chamber and pass into a hot cyclone. The cyclone separates the hot gas from the solids, which are reinjected to the combustion chamber via the return seal as explained above. The hot flue gas passes to a convective gas cooler, then to baghouse filters.

While there are over 25 circulating-bed combustors operating worldwide on low-grade fuels, there are currently no circulating-bed units operating commercially as hazardous waste incinerators. The developers have a pilot-scale unit in operation which is capable of incinerating a tonne per hour of hazardous waste. The company is also offering to construct commercial-scale facilities. A transportable incinerator is available for onsite demonstration projects [20].

Conclusion

As is pointed out in this paper, thermal treatment and destruction processes offer many advantages or management options for hazardous waste management. Existing processes can reduce waste volumes while meeting current environmental regulations. New processes now being developed or demonstrated offer stil more advantages for destroying especially hazardous or hard to combust material.

Given the restriction on land disposal operations currently under consideration by the EPA, thermal processes will continue to grow in popularity, and the less than one percent of the hazardous waste generation in the U.S. currently being managed through incineration will also grow.

References

1 S.K. Stoddard, G. Davis and H. Freeman, Alternatives to the Land Disposal of Hazardous Wastes: An Assessment for California, State of California Governor's Office of Appropriate Technology, Sacramento, CA, 1981.

2 EPA Hazardous Waste and Consolidated Permit Regulations, Part VII, Federal Register, May 19, 1980.

3 U.S. Federal Register, 40 CFR, Parts 264 and 265, Vol. 46, No. 15, January 23, 1981.

4 Guidance Manual for Hazardous Waste Incinerator Permits, US EPA/Mitre Contact Corporation, September 1982.

5 U.S. Federal Register, 40 CFR, Part 761.40, Vol. 44, No. 106, May 31, 1979.

6 Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (1972 London Dumping Convention), Intergovernmental Maritime Consultative Organization (IMCO), London, U.K., November 1972.

7 Mitre Hazardous Waste Control Technology Data Base — A Profile of Incineration Facilities, U.S. EPA Contract No. 68-03-3021, November 1982.

8 C.E. Brunner, Incineration System Selection and Design, Van Nostrand Reinhold, New York, NY, 1984.

9 Engineering Handbook for Hazardous Waste Incineration, SW-889, U.S. EPA, Office of Solid Waste, Washington, DC, September 1981.

10 R.A. Olexsey, Combustion of hazardous waste, In Combustion of Tomorrow's Fuels, Proc. Engineering Foundation Conferences, Davos, Switzerland, October 1984.

11 C. Castaldini, H.B. Mason, R.J. DeRosier and S. Unnasch, Engineering assessment report: Hazardous waste cofiring in industrial boilers, Report to the U.S. Environmental Protection Agency by Acurex Corp., June 1984, U.S. EPA Report No. 600/2-84/177a.

12 R.E. Mournighan, hazardous waste in industrial processes. Cement and Lime Kilns, Paper given at the First International Conference on New Frontiers of Hazardous Waste Management, September 1985, Pittsburgh, PA, EPA report No. 600-9-85-025.

13 Gin Watson, A proposed air resources board policy regarding incineration on an acceptable technology for PCB disposal, State of California Air Resources Board, Stationary Source Contract Division, Sacramento, CA, 1981.

14 Assessment or Incineration as a Treatment Method for Liquid Organic Hazardous Waste, US EPA Office of Policy Planning and Evaluation, Washington, DC, March 1985.

15 D.G. Ackerman, R.G. Beimen and J.F. McGaughey, Incineration of volatile organic compounds on the M/T vulcanus II, TRW Energy and Environmental Division, Research Triangle Park, NC, April 1983.

16 M.D. Jackson, J.F. McGaughey and D.E. Wagoner, At sea-incineration of PCB-containing wastes onboard the M/T vulcan I, U.S. EPA Report No. 600/7-83-024.

17 D.A. Oberacker, Hazardous waste incineration performance evaluations by the U.S. Environmental Protection Agency, Paper presented at the Energy Sources and Technology Conference and Exhibition, Dallas, TX, February 17—21, 1985, American Society of Mechanical Engineers, 85-PET-9, 1985.

18 Westat, Inc., National survey or hazardous waste generators and treatment storage, and disposal facilities regulated under RCRA in 1981, EPA Report No. 530-SW-84-005, OSW, Washington, DC, April 1984.

19 Assessment of Incinerations as a Treatment Method for Liquid Organic Hazardous Wastes, U.S. EPA Office of Policy, Planning, and Evaluation. Washington, DC, March 1985.

20 H.M. Freeman, Innovative thermal processes for the destruction of wastes, presented at the AIChE Annual Meeting, San Francisco, CA, November 25—30, 1984, AIChE Symp. Ser. 243, Vol. 81, 1985.

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